THE METASTABLE O2-$LiCoO_2$ AND $T^{\#}2$-$Li_{2/3}Co_{2/3}Mn_{1/3}O_2$ SYSTEMS

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Introduction

The O2-$LiCoO_2$ phase was obtained for the first time in 1982 in our group and it was shown that several structural transitions occurred upon lithium deintercalation, with especially the formation of a new O6-type oxygen packing. In the last few years, we have revisited this O2-Li_xCoO_2 system from a structural and physical point of view and we have also studied the manganese-substituted $T^{\#}2$-$Li_{2/3}Co_{2/3}Mn_{1/3}O_2$ system. A special interest has been devoted to the study of the phase diagram upon lithium intercalation and deintercalation in the structure. In the meantime, Paulsen, Dahn and coworkers have especially studied a series of manganese-based layered oxides $Li_{2/3}(M_yMn_{1-y})O_2$ (M = Li, Ni, Co) obtained by ionic exchange from the corresponding P2 sodium phases. On the contrary to the O3-$LiMnO_2$ also prepared by ionic exchange and characterised by a face centred cubic (fcc) oxygen packing, these layered manganese oxides do not convert to spinel upon cycling.

Results and discussion

In order to try to determine the mechanism of the P2 → O2 transition, the formation of O2-$LiCoO_2$ was followed *in situ* by X-ray diffraction. In a first step, only small O2 domains are formed into P2 crystals. Then, an oxidation reaction occurs, with the formation of the P2*-$Na_{\sim 0.5}CoO_2$ phase: it makes easier the Li/Na ionic exchange reaction. Since the ideal O2-type structure is obtained from P2 through gliding of one CoO_2 slab over two either by (1/3, 2/3, 0) or by (2/3, 1/3, 0), the possible formation of stacking faults was considered. Simulation of the X-ray diffraction patterns for the faulted O2 structures has shown that the growth of O2 is fast versus the nucleation of the O2-$LiCoO_2$ domains and, therefore, that O2-$LiCoO_2$ has an almost ideal oxygen packing. On the contrary, Lu, Dahn and coworkers have shown that structures with sometimes a high density of stacking faults are obtained for instance in the case of the $Li_{2/3}[Co_xNi_{1/3-x}Mn_{2/3}]O_2$ system.

The manganese-substituted $Li_{2/3}Co_{2/3}Mn_{1/3}O_2$ phase is characterised by a $T^{\#}2$-type structure, the oxygen atoms do not occupy, like in all other layered structures, the A, B or C positions of the same triangular lattice. Electrochemical cycling shows two potential ranges, the higher potentials being probably associated with the Co^{4+}/Co^{3+} redox couple and the lower potentials with the Mn^{4+}/Mn^{3+} redox couple. As for O2-$LiCoO_2$, several phase transitions occur upon cycling: an *in situ* X-ray diffraction study was thus performed in order to identify the different phases formed. A comparison of the phase diagrams versus lithium composition obtained for both systems will be given. A neutron diffraction study has shown that the lithium ions are distributed in very distorted tetrahedral sites (8e sites of the Cmca space group) in $T^{\#}2$-Li_xCoO_2 $(0.50 < x \leq 0.72)$. An electron diffraction study has also revealed for this phase several superstructures resulting from lithium/vacancy orderings. Due to very close energies, these structures can coexist in the same crystal or even lead to the formation of incommensurate superstructures. A special interest has also been devoted to the study of the reversibility of the Li // O2-Li_xCoO_2 and Li // $T^{\#}2$-$Li_xCo_{2/3}Mn_{1/3}O_2$ systems. Irreversible structural transformations occur for the second one upon cycling.

Acknowledgments

The authors thank C. Denage and P. Dagault for their collaboration, ILL for the neutron diffraction experiments and CNES and Région Aquitaine for their financial support. National Science Foundation International Research Fellow IRF 0000-429 is also gratefully acknowledged.